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POLYCYCLIC AROMATICS IN SURFACE AND GROUND WATER

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(Polyzyklische Aromate in Oberflächen- und Grundwasser)

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POLYCYCLIC AROMATICS IN SURFACE AND GROUND WATER

Several hundred related compounds belong to the group of polycyclic aromatics, part of which is more or less largely carcinogenic when applied to the skin, injected or dissolved in the food of experimental animals. The most known substance is 3,4-benzopyrene, of which K.H. Bauer has said it is the substance of fate for humanity. Whether this emphatic statement can be upheld is questionable, since, by way of example, the percutaneous administration of benzopyrene to voluntary experimental humans in the USA did not lead to tumors. On the other hand, its harmlessness is in no way proven; above all it is necessary to take the aerogenic and peroral application into account.

On this basis it is necessary to concern ourselves with the load on man from various sources. In regard to water, efforts go back to the research of Wedgwood and Cooper. In 1954, the authors analyzed - starting with the knowledge of the presence of aromatics in tar - the waste water in gas works and found, admittedly only qualitatively, benzopyrene and other polycyclics. Our own research, done in 1959, showed that aromatics in water have not only an industrial origin, because benzopyrene was also detectable in untouched nature, and a main source proved to be household waste water.

I. Presence of polycyclic aromatics in water

In the beginning of our research, we assumed that the presence of polycyclics in water is related to the simultaneous presence of fats, oils or detergents, or that they enter the water by means of solid particles, such as soot. Research on particles therefore comprised the first part of the program. We examined, for example, filter mud from a Lake Constance water works and found in addition to benzopyrene also 1,2-benzoanthracene, 3,4 and 10,11-benzofluoranthene, and indeno-pyrene among other aromatics. The amount of carcinogens constituted several milligrams for every kilogram of the mud. In centrifugates of the Middle Rhine, almost the same amounts of cancer-causing substances were detected, but the Rhine contained 200 times higher amounts converted into the water volume. Comparative analyses showed then, that it is not only a matter of the amount of sedimentation-producing particles per cubic meter of river water. One cannot simply use the appearance of the river as a basis for evaluation; far more decisive is the nature of the waste water fed to it. Shipping, however, proved of secondary importance as a source, aside from oil accidents.

We obtained a further indication of the possible origin of carcinogens in the microscopic examination of filter mud, in which many diatoms were found. On the strength thereof we fished phytoplankton out of Lake Constance, but found only 1/10 of carcinogenic concentrations in the filter mud. The

main portion is therefore obviously adsorbed with the rest of the particles. Since these consist mainly of dust and soil, we expanded on the research of Blumer on the presence of polycyclics in ground soil. Aside from 3,4-benzopyrene, there were overall up to 30 different polycyclic aromatics in the ground tests. This and analyses by other authors resulted in the collective data in Table 1. (Due to the various methods of detection the findings must be limited to 3,4-benzopyrene.

Table 1 shows that the lack of 3,4-benzopyrene in the ground is a rare exception. In uncultivated soil, an average of 1-10 µg/kg must be estimated and in fertilized areas, 100 µg/kg.

Similar orders of magnitude and in part even considerably higher amounts were measured in such areas which had considerable pollution due to aerosols in the air. But 3,4-benzopyrene is not only detected in surface layers; we found aromatics also in a 100,000 year-old bore hole from a depth of 170 m, i.e. certainly not a substance due to civilization.

The main sources of aromatics in surface water are certainly street dust fallout. Bitumen and tar street dust contain up to a half gram of carcinogens per kilogram, or expressed comparatively, 100 times more than sea water centrifugates.

The decisive effects on water obviously begin with the amount of waste water. Here also, it is a case of aromatics

Table 1: 3,4-Benzopyrene in Surface Ground Tests

		µg 3,4-benzopyrene/kg	Author
I.	Protected water area	0	Shabad 1968
	uninhabited areas (Iceland)	0 - 5.8	Grimmer et al. 1972
II.	Heath sand	0.5	Borneff & Kunte 1963
III.	Forest soil	40 -1300	Blumer 1961
		1.5- 4.0	Borneff & Fischer 1962
		1.5- 2.5	Borneff & Kunte 1963
		2 - 170	Mallet & Heros 1962
		0.1- 6.0	Shabad et al. 1971
IV.	Soil outside of settled areas	2 - 127	Shabad et al. 1971
V.	Garden soil	90	Blumer 1961
		22 - 939	Zdrazil & Picha 1966
		12.8	Shabad et al. 1971
VI.	Soil from residential areas (old)	270 - 350	Shabad 1968
	(new)	81 - 104	Shabad 1968
VII.	Arable soil	900	Blumer 1961
		3.3- 82	Borneff et al. 1973
VIII.	Soil near railroads	312 -2040	Zdrazil & Picha 1966
	highways	29	Shabad 1968
	highways	15.8- 66.8	Shabad et al. 1971
IX.	Soil from airport areas	11.9- 68.0	Shabad et al. 1971
		785 -	Grimmer et al. 1972
X.	Soil from oil refineries	200 000	Shabad 1968

as corpuscular elements. We concluded that from the purification effect of treatment plants, which can be estimated at a third each for the mechanical processes and biological structure.

According to this research, raw water contains up to 50 mg and more of carcinogens per m^3 in corpuscular form.

However, polycyclic aromatics do not only appear in water in corpuscular form; we found them also in a dissolved state. We originally thought of an aiding factor from substances active on the boundary surface, but it was soon apparent that the concentrations of detergents necessary herefor are not present at all in the rivers and lakes. With the refinement of analysis techniques, it was discovered that even without the presence of surface-active agents and mineral oils, polycyclics are dissolved in pure ground water.

We can assume today that precipitation, in so far as it does not already contain aromatics from aerosols, dissolves traces of these compounds from the ground and bring it into the ground water by way of leakage. Analyses verify that all ground water therefore bears a normal level which lies in the order of magnitude of 10-40 $\mu g/m^3$ when the following compounds are taken as a basis: fluoranthene, 3,4 and 11,12-benzofluoranthene, 3,4-benzopyrene, 1,12-benzoperylene and indenopyrene.

In addition, it should be mentioned that the improved ground water, therefore the main water, does not correspond in every case to the contents of carcinogens in well water. We obtained this result in a research series in which we tested the well of a gallery separately and additionally examined its mix water. Here the amounts were almost 10 times

as high as in the well itself, i.e., the increase must have occurred in the supply network. In the first place, the cause must be considered in the insulating layers. Even though, according to our research, the bitumen in the water main construction contained a few milligrams of carcinogens per kilogram, further research showed, however, that measurable amounts still appear in the water and that these emissions last several months in every case.

Surface water is exposed to the described additional pollution by means of sedimental aerosols, dust from street surfaces and different waste water, so that considerable concentration increases are possible. Comparisons showed that on the average a small amount of polluted river or seawater contains 5 times more aromatics than ground water , while moderately polluted river water is perhaps 10 times more heavily loaded and waste water 10,000 times.

As an example is the result of section research of the Rhine, conducted twice.

Table 2 shows on the one hand the increasing pollution (first from Rheinfelden as well as a second increase in the Mainz area) and on the other hand a proportionate aromatic concentration in the Middle and Lower Rhine. Such findings point to gradual loads due to civilization, whereby it probably has to do with local waste water introduction. Also, on the contrary, dilutions by less loaded tributaries play a role.

Table 2: Polycyclic Aromatics in $\mu g/m^3$ of Rhine Water

River - km Fluß km	Place Ort	Nov. 26-28 26.-28.11.1969	Feb. 2-4 2.-4.2.1970
30	Stein a. Rhein	31	–
149	Rheinfelden	385	–
170	Weil a. Rhein	274	–
293,5	Kehl	126	–
362	Maxau	274	–
415	Altrip	279	–
480,6	Oppenheim	946	–
494	Weisenau	–	473
527,2	Bingen	3.610	802
584	Oberlahnstein	13.374	1.273
641,3	Rolandseck	9.629	1.531
688,9	Köln	980	3.465
772	Duisburg	685	4.916
852,6	Emmerich	1.018	5.682

In the considerations relating to the causes for the fluctuations, we also included precipitation.

It is easy to assume that rainfall leads to increased fallout, of the soil, street dust, soot, etc. Further, another phenomenon comes under consideration, which we also found in our pesticide analyses, namely the whirling up of sedimentary mud in the river bed.

We verified this phenomonon once again in the Rhine.

Figure 1 shows that at low water the aromatic load was in the range of 20 kilograms per day and that it increased to almost 80 kilograms when the discharge was doubled, whereby the maximum high water peak was reached. It is not, therefore - as frequently suspected - a question of a thinning out of the harmful substance by precipitation, but a worsening of the situation. We assume that it is rain overflow in

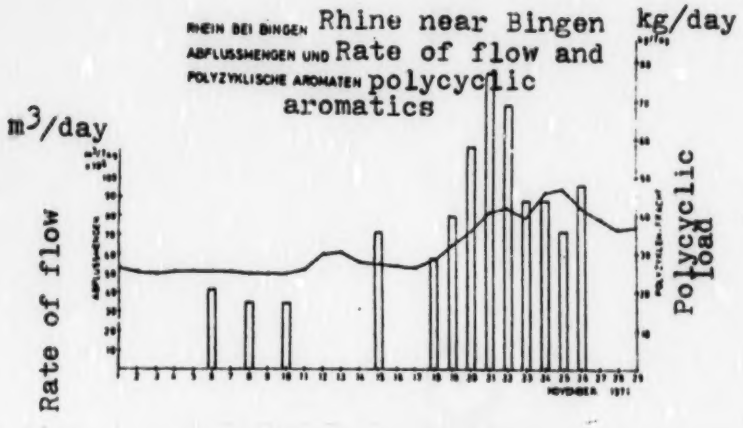

Figure 1: Polycyclic aromatics in the Rhine at Bingen in relation to the water flow

particular in the purification plants which is responsible.

The results show clearly how far we are from an efficient water protection system; since on the average the aromatic concentrations in the high load area of the Rhine lie perhaps over 100 times that of the rate of flow from Lake Constance. Rivers such as the Danube and the Main are not much less polluted and even in several small streams there were considerable aromatic concentrations.

However, surface water can, on the other hand, be equal to ground water in quality with careful protective measures.

Figure 2 shows that in sea water (surface) in the summer, autumn and winter, there were the same ground water concentrations. An increase occurred only during the spring, i.e., the water quality obviously suffers particularly during the melting of the snow by the introduction of winter aerosols

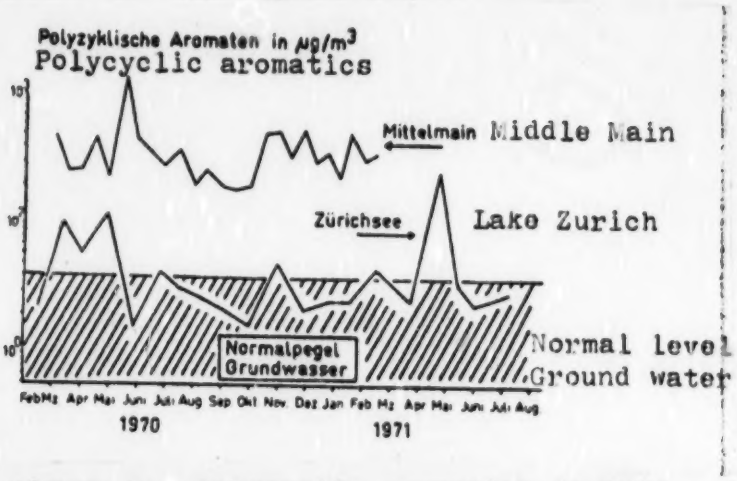

Figure 2: Polycyclic aromatics in Lake Zurich

from heating, vehicles and industries. There was no proof of the influence of full circulation or algae growth.

The increase in concentrations in the spring, considered in the absolute, must however be considered as insignificant. They are of no importance for the drinking water supply of the population.

It can be said in summary, concerning the presence of polycyclic aromatics in water, that even pure drinking water does indeed contain a very small amount and that civilization can generate an increase up to 10^5 times that. Above all, household and industrial waste water has contributed an effect here, and further, street dust and oxidation products.

II. The significance of polycyclic aromatics in water

The general presence of carcinogenic substances in water

must necessarily lead to the question of hazards in man. It can be established that, considering the two most important viewpoints, the dose and the specific sensitivity, the consumption of ground water with the inevitable carcinogenic content of a few nanograms per liter in itself cannot lead to cancer. The quantities are too small for that. The problem, however, must be evaluated from the view of the river water treated for drinking water, and particularly with regard to syncarcinogenesis, i.e., the interaction of carcinogens from the most different sources. At the same time, the carcinogen content of the other foodstuffs should be questioned. In a rough estimate of the yearly total dose, it must be considered that vegetables contain 3-4 mg, vegetable fats and oils 0.1 mg, smoked meat and drinking water 0.05 mg each. Animal food, which is eaten raw, cooked or roasted, contains in comparison hereto no carcinogens to be considered. The total yearly dose from known pure sources is in the order of magnitude of approximately 1-10 mg, with a 3,4-benzopyrene content of 0.1-1.0 mg.

For the evaluation of this quantity, it can be said that 100% of the test mice die from carcinoma 18 months later, at the most, when 1 mg of 3,4-benzopyrene is applied to the skin (Müller). Also, considerably smaller doses still have an effect, though of course the latent period increases with decreasing tumor frequency. However, this high carcinogenicity

only applies in regard to administration to the skin. In feed, a considerably higher dose is needed. Since the histological composition of the gastric mucosa varies widely, the carcinogenic hazard to man can only be largely estimated with the aid of such animal experiments. By way of example, a direct conversion of the dose in relation to body weight is not admissible, since the sensitivity of the species would then remain completely out of consideration. A further significant uncertainty comes from the fact that with the diet there is also a mixture of different polycyclic aromatics from active and inactive compounds ingested. There should be a series of publications on the interaction of carcinogenic substances, and the reciprocal output and inhibition of active and inactive aromatics, respectively but the findings are not yet satisfactory. Obviously the synergistic as well as the antagonistic effect, respectively, depend not only on the nature of the substances, but also on the mixture correlations and the total dose. These relationships are being tested at the present time in the Mainz Hygiene Institute on a large group of animals. Efforts toward an interim evaluation have not produced any usable results as yet.

A general evaluation is also complicated due to the individually different benzopyrene hydroxylases production in the human intestine. Here the ingestion of a mixture of aromatics will also have a different effect from the intake

of a pure substance. From our in vitro research (Kunte), it can be concluded that the mutual effect of relatively large amounts of inactive substances concurrently uses up the benzopyrene hydroxylases, whereby the activity of 3,4-benzopyrene, etc., are more or less maintained. Since fluoranthene as such an inactive compound almost always appears in abundance in the aromatic mixture, this finding can be of practical significance. However, the question remains how the body adapts to a continuous intake.

Apart from the establishment of the degree of danger still open on this basis, the demand for the elimination or at least the limitation of carcinogens in foods is, however, significant and justified. Although the dose ingested with drinking water doesn't take precedence, protective measures are also indicated here, since it is a question of a non-replaceable product, for which there is no possibility of choice.

The elimination of aromatics is necessary, however, on a second basis: namely a lower content in the water indicates the absence of unappetizing substances.

As a general principle it can be added that the elimination or limitation of undesired substances in drinking water is assured partly by their direct determination, but also partly by indicators. The classic example of the latter case is the estimation of risks of intestinal infections by

detection of entercolitis and enterococcus. Also the hygienic pure quality in the sense of its taste is guaranteed by the determination of indicator substances. In passing, it is suspected that in this sector, considerable progress can be made when the indirect, mistake-ridden coli-method can be replaced by direct proof of a fecal specific substance, that of coprosterol. For the detection of the amount of organic substances, the determination of the total carbon is doubtless of significance. For the detection of the amounts in waste water and the abundant removal of waste water contents of organic nature, respectively, in the treatment of drinking water, the polycyclic aromatics can be successfully introduced. Above all, this method has the advantage of great sensitivity. While with the use of $CMnO_4$, the correlation of drinking water to river water containing waste water is around 1:20, for polycyclics such a correlation is figured from 1:100 to 1:1000.

In order to consider both viewpoints in practice, assurance of pure treatment and elimination of potential harmful substances, a reliable and easy method of detection is required. Analysis covers 6 typical polycyclic aromatics (fluoranthene, 3,4 and 11,12-benzofluoranthene, 3,4-benzopyrene, 1,12-benzoperylene and indenopyrene). If it were limited to only one substance, perhaps benzopyrene, there would hardly be any control possibility in accidental contamination of the test or the instruments with the same

compound.

After the results of the analyses up to now, we consider 50 $\mu g/m^3$ as the normal level of the 6 polycyclics in ground water, and 100 $\mu g/m^3$ in main water. Drinking water with more than 150 $\mu g/m^3$ can be classified as "possibly contaminated," and correspondingly screened. Water with more than 200 $\mu g/m^3$ (=0.0002 mg/l) should be rejected as "impure." The limit allows for the standard deviation of the method, so that erroneous evaluations are practically excluded. In this form, the new drinking water standards of WHO have been accepted. For the exclusion of unjustified objections, we have set the limit relatively high; as soon as there is an extensive compilation of data, a possible lowering of the standards can be considered.

III. The removal of polycyclic aromatics

The rule should be to give preference to those methods for the removal of carcinogens in water which, aside from their usefulness for conventional functions, simultaneously have good effectiveness in the elimination of aromatics. In this manner, additional costs are avoided. There are various reports on the effectiveness of the usual methods for the treatment of drinking water. For example, Graf and Nothafft conducted research in 1963 on the question of whether by means of the usual treatment with chlorine gas, perhaps dissolved carcinogens are destroyed and become

ineffective. They came to the conclusion that in practice not too much should be expected. Traktman and Manita obtained in 1966 similar results with similar research. Nevertheless, we found in our analyses of Lake Zurich water, during the last two years, in accordance with primary chlorination of raw water with perhaps 1 mg/l, a benzo-pyrene reduction of around 70%. In 1968 Reichert reported his results with chlorine dioxide. Within the first 2-3 hours, over 90% of the introduced benzo-pyrenes had been broken down to exclusively inactive products. With decreasing benzopyrene concentrations, the half-life periods increased, and from less than 10 ug/m^3, then ClO_2, even with a considerably longer reaction time, no longer had an oxidation action. From the standpoint of hygienists, however, these low concentrations are still objectionable.

The increasing introduction of ozone led Reichert to further experiments which showed that with O_3, the conversion of aromatics was faster and as a rule also progressed to a higher oxidation degree than with ClO_2, but this advantage was cancelled out by the susceptibility to reaction problems. The use of ozone necessitates, therefore, an effective preliminary purification if a satisfactory elimination of carcinogens is to achieved in practice.

Aside from chemical methods, physical purification comes under consideration. In 1962, we conducted our first

A-carbon analyses of the Schierstein Rhine water treatment plant. This and further research finally led to the knowledge that the A-carbons measured in the total contents of polycyclics were 90% eliminated. Nevertheless, it is only possible to reduce the higher carcinogenic concentrations when the amounts lie in the range of the normal level in the ground water and are not affected by scientifically justifiable efforts. We have again tested the practical methods in laboratory experiments (Reichert et al.) and found that the various kinds of A-carbons do not have the same value and that the individual polycyclic aromatics are adsorbed at various rates. After a sufficient contact time, even partial desorption phenomena appear. The effectiveness was in no case under 99%. The lesser effects in practice could be based on the fact that in the mean value the gradual depletion of adsorption ability enters in. In the laboratory, only fresh carbon was used. There are no sufficient practical experiences yet on the suitability of artificial granulates (Scholz).

Sedimentation plays an important role not only in purification of waste water, but also in the treatment of drinking water. In regard to the removal of carcinogens, we obtained indications on the effect of such receiving basins in the water recovery plants of Wiesbaden-Schierstein: the carcinogen concentration was in the range of 10% of that of the Rhine water, after circulation of several hours.

Findings on the effectiveness of filtration we first acquired in the Sipplingen water works. There, the Rhine water, after purification by means of rapid sand filters, contained only 25% of the carcinogens in the untreated water of Lake Constance. We further compared the water from the Elbe in Hamburg with the water from 2 experimental wells, which required a mixture of pure ground water and filtrates from the river bank. In the first well we found 35% and in the second still 13% of the polycyclic concentration of the Elbe. The water in the first well was additionally treated by means of aeration, rapid and slow sand filtration; 6% remained. In the Zurich water works, however, there were findings, as with ClO_2 and A-carbons with the slow sand filtration: the carcinogenic concentration in the range of the normal level showed no further reduction. Analyses of river bank filtration on the Danube, with flowing times of 21 days showed decreases in aromatic concentrations by half or two thirds. In general, the research shows that by means of mechanical purification of surface and waste water by sedimentation or sand filtration, perhaps 2/3 of the polycyclic aromatics can be removed. In so far as in a single case greater effectiveness can be ascertained, it must be assumed that the correlation of corpuscular to dissolved carcinogens was greater than 3:1.

In the flocculation plants, dirt particles suspended in water were converted into aggregates capable of sedi-

mentation and were separated by means of gravitation and/or subsequent filtration. As a rule, a high chlorination follows simultaneously, so that, overall, far-reaching elimination of dissolved and also corpuscular carcinogens present can be expected. We conducted the first supervision of such a plant in 1963 in Wiesbaden-Schierstein. After flocculation and filtration, the Rhine water contained, as opposed to the inflow from the sedimentation basin, now only 9 instead of 20 polycyclic aromatics; their total amount had been reduced to almost half and carcinogenic components reduced to 10%.

In the semi-technical experimental plant of Leipheim on the Danube, further analyses were done from May 1966 to April 1968. This research showed that the flocculation treatment in fact does lead to a significant reduction in carcinogens. After flocculation, the water still contained an average of 10% and after filtration 5%. With optimal application and particularly with a proper secondary dosage of ferric chloride and ozone, there was a residual content of polycyclics which corresponded to the normal level of these compounds in ground water.

In addition, we were recently able to conduct comparative research on the effectiveness of various flocculation methods in a semi-technical plant. Tested were iron chloride, aluminum sulphate and ferri-floc. With a relatively small concentration in raw water of around 50 µg of

of aromatics/m^3, the result was a purification effect in the range of 90%, whereby ferri-floc and aluminum sulphate were slightly above the iron chloride.

IV. Summary

Carcinogenic polycyclic aromatics belong to the chronically effective harmful substances in drinking water, which are partly from natural origin and partly caused by pyrolytic processes. Since they appear in particularly high concentrations in waste water, they are significant as pollution possibilities. Their elimination from drinking water is necessary, although a small residual content of polycyclic concentrations in ground water can be tolerated. In river water, a third of the aromatics appear in corpuscular form, a further third is finely dispersed and the rest actually dissolved. In modern treatment plants, two thirds of the aromatics can be eliminated by means of sedimentation, flocculation and filtration, the rest can be reduced by oxidation or A-carbon treatment to harmless residuals. The effectiveness of individual treatment stages was established by laboratory tests and research on a semi-technical scale. Control analyses in various water works assured the effectiveness of the treatment in practical operation.

It is our view that aromatics analysis represents a significant supplement to the customary research of

drinking water; its application is also recommended by the WHO to assure the good taste and harmlessness of water.

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